

Determination of Polycyclic Aromatic Hydrocarbons (PAH) from Air Conditioning Dust in Bonny Metropolis

Abbey, D.M.^{1*}, Dibofori-Orji, A.N.² & Ihunwo, O.C.³

¹⁻³Department of Chemistry, Faculty of Natural And Applied Sciences, Ignatius Ajuru University of Education, Rumuolumeni, Rivers State, Nigeria. Corresponding Author: abbeydabebara@gmail.com*



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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants that are mostly carcinogenic and mutagenic at low concentrations. They have pyrogenic, petrogenic, geogenic, anthropogenic, and industrial sources. PAHs bound in dust retained in air-conditioning unit filters from office and residential buildings in Bonny metropolis were analyzed using a Gas-chromatography Mass spectrometer. The average summation PAH (Σ_{PAHs}) in Bonny's office and Bonny's residential, areas were 39.52 and 21.14, mg/Kg respectively. Principal PAHs in Bonny Metropolis were acenaphthalene and naphthalene. Furthermore, carcinogenic summation ($\Sigma cPAH$) from Bonny office and Bonny residential, areas were obtained as 14.87 and 8.10 mg/Kg respectively. PAH ratios such as low PAH over high PAH (LPAH/HPAH), Fluoranthene plus Pyrene FL/(FL + PYR), Anthracene plus Phenanthrene ANT/(ANT + PHE), Benz[a] anthracene plus Chrysene BaA/(BaA + CHR) across the metropolis depicts that the source of these contaminants are petrogenic and anthropogenic. Bonny metropolis tends to have higher PAH contaminants and high carcinogenic contaminants. This could be attributed to the dense industrial activities and uncontrolled emissions within the metropolis. Thus, the government should establish and enforce environmental regulations that curb industrial emissions within the studied metropolis.

Keywords: Molecular diagnostic ratios, Concentrations ratios, Chromatography, Air quality, Particulate matter, Ibadan, Pyrogenic source.

Introduction

The understanding of the complexity of environmental problems in the 21st century and the necessity to protect our planet has become one of the most crucial and timely tasks facing mankind. The troubling phenomena over the decades include climate change, ozone layer depletion, increasing intensity and frequency of natural disasters, a decrease in biodiversity, deforestation, desertification, progressive soil acidification, salinization and erosion, poor air quality, and water pollution.

Humans have altered and strived to control natural processes to improve their quality of life. It has often led to the opposite effect and resulted in deterioration of human health and disruption of environmental equilibrium. As more countries have become industrialized and urbanized, pollutants are reaching disturbing levels. In recent decades, public awareness of the toxicity of polycyclic aromatic hydrocarbon poisoning is growing even in developing countries. Pollution is considered the release of unwanted substances to the environment that damage and adversely affect a man and his environment (Tripathi *et al.*, 2007). Polluted air contains one, or more, hazardous substances which are particulate matter such as PAHs (EPA, 2009).

Air pollution (indoors and outdoors), is a worldwide recognized threat to the health of humans, even at low doses, since it has been, beyond any doubt, associated with many effects on human health, including increased mortality and morbidity rates but also with ecosystems damage, impacts on the built environment and the climate (EEA, 2017; Oliveira *et al.*, 2011).

The World Health Organization (WHO) estimated a total of 12.6 million deaths in the world due to unhealthy environments representing 23% of total global mortality and 26% of deaths in young children (Landrigan *et al.*,

2017). Some air pollutants can persist for long periods and accumulate in the environment and food chain, thus affecting humans and animals via multi-route of exposure (inhalation, dermal, ingestion).

In urban areas, air conditioning unit (AC) has become increasingly important and is used in most households for cooling, heating, or dehumidifying indoor spaces; in addition to improving the quality of indoor air, and helping to filter particulate pollution from indoor air (Yu *et al.*, 2019; Ali *et al.*, 2018). Indoor and outdoor air quality is closely related to the exchange process, with indoor air purified by AC filters when outdoor air is circulated into the residence (Yu *et al.*, 2019). The residue of AC filters is majorly made up of dust particulate. Most people are aware that outdoor air pollution can damage their health, but not so informed that indoor air pollution can also have significant effects as well (Manisalidis, 2020). Over the years, dust contamination has received much attention as a source of polycyclic aromatic hydrocarbon contamination around the world (Saeedi *et al.*, 2012, Wang *et al.*, 2017). Dust released into the atmosphere from industrial plants (especially smelters and refineries) and mines frequently contains large amounts of toxic metals, polycyclic aromatic hydrocarbons and produces a huge quantity of waste (Balabanova *et al.*, 2012), other major contributors to the overall amount of dust are cement works, ferrous and non-ferrous industries, petrochemical industries, coal combustion, scrap metal recovery and ceramic industries (Davis and Gulson, 2005). The growing rate of industrialization is gradually leading to contamination and deterioration of the environment and pollution is likely to reach disturbing levels in the years ahead. PAHs are a major pollutant and public concern over the deleterious effects of PAHs has grown rapidly due to recognition of their toxicity, carcinogenicity, and teratogenicity. Benzo(a)pyrene (BaP) possesses the greatest carcinogenic potential among the various PAHs (Pongpiachan *et al.*, 2013).

Polycyclic aromatic hydrocarbons (PAHs) are aromatic hydrocarbons with two or more fused benzene rings in various structural configurations arrangement (linearly, angularly, or in clusters) (Loganathan *et al.*, 2014; Ong *et al.*, 2007). PAHs containing up to four rings are referred to as light PAHs and those that contain more than four rings are heavy PAHs. Heavy PAHs are more stable and more toxic than light PAHs (Wang *et al.*, 2017).

Concentration ratios of specific pairs of PAHs are widely used for the qualitative determination of the PAHs sources. These ratios are called PAHs molecular diagnostic ratios and are commonly used for PAHs concentrations in air, soils, and sediments. The application of PAH diagnostic ratios has been reviewed in their use by environmental researchers for the identification of PAHs pollution emission sources (Teng *et al.*, 2012; Sun and Zang 2013; Rajpara *et al.*, 2017; Xing *et al.*, 2016). The ratios apply to PAHs found in different environmental media: air (gas + particle phase), water, sediment, soil, as well as biomonitor organisms such as leaves or coniferous needles, and mussels. Numerous studies show that diagnostic ratios change in value to different extents during phase transfers and environmental degradation.

PAHs released into the environment may originate from many other sources; including gasoline and diesel (Zhang and Balasubramanian, 2016), fuel combustion, and tobacco smoke. PAHs are detected in the air (Halse *et al.*, 2015), soil, and sediment (Blumer *et al.*, 1977). The major route of exposure to PAHs in the general population is from breathing contaminated ambient indoor air, eating food containing PAHs, smoking cigarettes, or breathing smoke. PAHs in agricultural crop leaves contribute to the exposure of organisms to these chemicals through the

dietary pathway (Harvey, 1997; Wang *et al.*, 2017). PAHs are frequently measured in the atmosphere for air quality assessment.

A series of health problems (an increased risk of skin, lung, bladder, and gastrointestinal cancers) for workers exposed to mixtures of PAHs chemicals have been reported such as BaP and Pyrene have been identified as the cause of cancer in laboratory animals (Armstrong *et al.*, 2004; Diggs *et al.*, 2011).

Generally, sample pre-treatment comprises (1) solvent extraction of PAHs from filters and sorbents; (2) extract concentration; (3) some form of liquid, or solid, chromatography clean-up; (4) eluent concentration; and (5) injection into gas chromatography (GC) for analysis. Extraction agents that have been studied, include surfactants, biosurfactants, microemulsions, natural surfactants, cyclodextrins, vegetable oil, and solution with solid-phase particles. These extraction agents have been found to remove PAHs from the soil at percentages ranging from 47 to 100% for various PAHs.

PAH from water samples into a rotating-disk microextractor and the subsequent determination by gas chromatography-mass spectrometry. Shamsipur *et al.*, (2015) prepared and evaluated a novel solid-phase microextraction fibre based on functionalized nanoporous silica coating for extraction of PAHs from water samples followed by GC-MS detection. Other extraction methods followed by GC-MS, HPLC-FLD, or other analytical instruments include Supercritical carbon dioxide solvent extraction (Laitinen *et al.*, 1994), and thermal extraction coupled with GC/TOF/MS (Liu *et al.*, 2002).

White *et al.*, (2015) examined indoor air pollution from the use of indoor stoves and/or fireplaces as an important source of ambient PAHs exposure. The risk of breast cancer was increased among women reporting ever-burning synthetic logs, but not forever burning wood alone. Verma *et al.*, (2015) described the concentration and emission fluxes of PAHs emitted during the burning of commonly used indoor materials, i.e., 15 fuels (i.e., biomass (BM), coal (C), cow dung (CD), kerosene (K), 4 incense (IS) and mosquito coil (MC) in Chhattisgarh, India. The concentration of total 13 PAHs (ΣPAH_{13}) (i.e., phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)-pyrene, dibenz(ah)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, and coronene) of particulate matter (PM_{10}) in the indoor air were reported. The mean concentration of the ΣPAH present in an indoor environment is much higher than the WHO limit value of 1.0 ngm^{-3} . The sources and toxicities of PAHs were also discussed.

Hsu *et al.*, (2015) conducted PAHs measurements at four communities of ambient Air quality in Canada. Their findings pointed to the potential importance of localized water-air and/or surface-air transfer on observed PAH concentrations in air. Vuković *et al.*, (2014) performed a study in four parking garages intending to provide a multi-pollutant assessment. PAH is an important pollutant contained in black carbon that is widely studied due to possible cancer and non-cancer risks it poses to its receptors, particularly humans. Particulate soot is formed after incomplete combustion of carbon containing materials according to Niranjana and Thakur (2017) who regarded it as an unwanted powdery mass of fine black particles. Gas-phase soot contains polycyclic aromatic hydrocarbons (Omidvarborna *et al.*, 2015). Oloyede and Ede (2020) also determine the concentration of PAH in air samples in Port-Harcourt metropolis, Nigeria revealing a total concentration range of 0 to 9,589 mg/kg in the rainy season and

0.46 to 131mg/kg range in the dry season. Furthermore, Benzo(a)pyrene equivalent (BaPeq) analysis showed that benzo(a)pyrene, DiBenzo(a,h) anthracene, and Indeno (1.2.3-cd) pyrene contributed the highest cancer toxicity with 94% and 85% in wet and dry seasons, respectively.

Scientific researchers have reported the urgency for consistent monitoring of the safety of the environment owing to the continuous addition of unwanted substances into the environment. This study area has been reported to be densely polluted which is evident in the presence of a large amount of soot. Moreso, the chemical composition of particulate air pollutants in the study area has not been explored considering indoor activities and the nature of air available within offices and residential areas. However, there are several approaches to sampling in evaluating indoor air quality which reflect air pollutant exposure's effect. Thus, the dust collected on the HVAC filters should provide information about the outdoor and indoor air quality of the study area, and the study aimed at determining the PAHs from air-conditional dust in offices and residential areas in Bonny metropolis.

Methodology

Study of the Area

The study area is Bonny local governments area in Rivers State due to the heavy presence of multinational companies operation. Bonny Island lies about 40 kilometers south of Port Harcourt. It is the administrative headquarters of Bonny Local Government Areas in Rivers State (Fig.1).

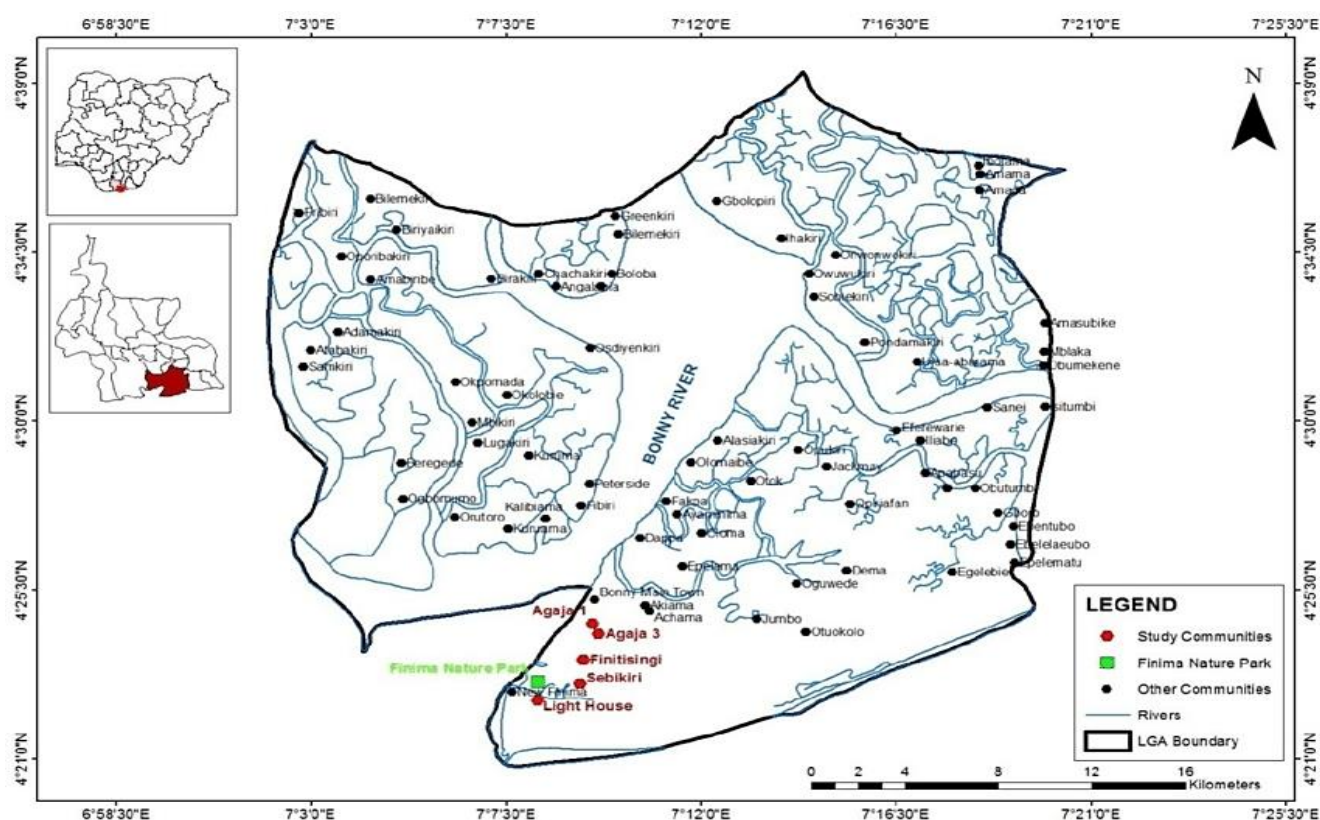


Fig.1. Mapping of Sampling Locations within Bonny Metropolis

With latitudes 4°52'N and 5°02'N, and longitudes 6°56'E and 7°04'E, with a population of 270,000 people (NPC, 2006). The Island has a rather flat topography, with an elevation of 3.05 atmospheric mean sea level and a total land

area of 214.52m² (NLNG, 2005), with tidal floods and land subsidence affecting around 70% of its size. Ibani is the local language on Bonny Island. The island is directly connected to the Atlantic Ocean, where giant oil tankers export crude oil. According to previous studies, the seasonal fluctuation of rainfall in the Niger Delta ranges from 2301 to 3670 mm during the wet season (March to November) and 43 to 97 mm during the dry season (December to March) (Adejuwon, 2012).

Samples Extraction and Analysis

HVAC Filter Dust was brushed into an air-tight Polyethylene bag, packed, and stored at temperatures below 4°C, for a maximum of 7 days before digestion and extraction, and 40 days after extraction before analysis. Ten grams (10g) of the sample were carefully weighed into a dried organic free and chromic acid pre-cleaned extraction bottle, ten grams (10g) of anhydrous Sodium Sulphate were added and mixed. 30ml of Dichloromethane was added to the mixture and thoroughly mixed with a glass rod. The sample was placed in an organic flask shaker at 500rev/min for 30mins. The extract was filtered and the filtrate was left in the extraction bottle at laboratory room temperature to concentrate for a minimum of 24 hours until about 2ml of the concentrated sample was left in the extraction bottle for separation into aliphatic and aromatic fractions using Dichloromethane and n-Hexane respectively. Rotary evaporators were used to concentrate aromatic fraction to approximately 1.0 ml and stored in dried organic free and chromic acid pre-cleaned glass vials with Teflon rubber caps and refrigerated at -4°C until analysis and standard reference method (fig.2) for PAH analysis was EPA8015-GC/MS, prepared by the manufacturer.

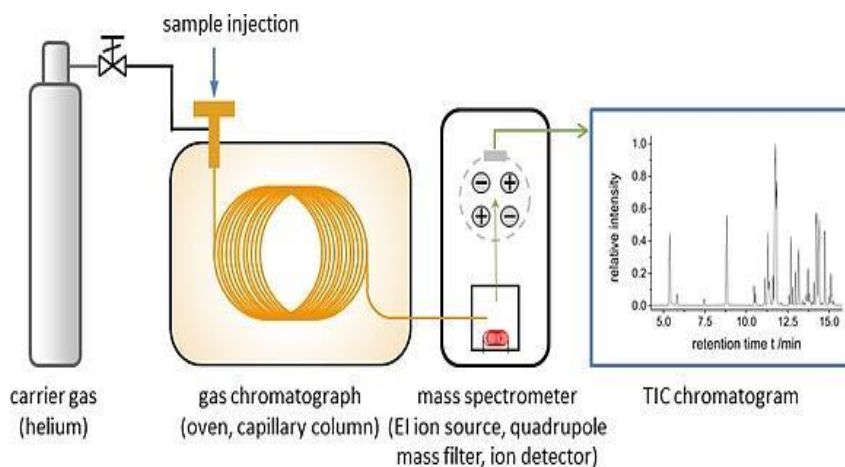


Fig.2. The principle of GC/MS Instrumentation (Jones, 2019)

Statistical Analysis

It involves Summation, mean and standard deviation using Microsoft excel 2016, Statistical Package for Social Sciences (SPSS). Pearson's correlation and Paired Sample T-test were conducted to study the significance of principal components across the sampling locations. In all cases, the level of significance was taken to be $p < 0.05$.

Result and Discussion

The concentration of polycyclic aromatic hydrocarbons content present in HVAC filter dust from office and residential sampling sites in Bonnymetropolis, using a Gas Chromatography-Mass Spectrometer is presented in Table 1 below. The results are expressed in mean and standard deviation of concentration in mg/kg.

Table 1. Polycyclic Aromatic Hydrocarbon (PAH) Content Concentration of HVAC Filter Dust Particulate in Bonny metropolis

PAH Components	No. of Rings	PAH Concentration (mg/kg)	
		Office	Residential
Naphthalene	2	4.276 ± 0.129	2.791 ± 0.332
Acenaphthalene	3	4.223 ± 0.098	4.481 ± 1.682
Acenaphthene	3	4.064 ± 0.160	3.104 ± 0.06
Flourene	3	ND	6.661 ± 0.000
Phenanthrene	3	4.303 ± 0.237	3.00 ± 0.05
Anthracene	3	3.974 ± 0.140	2.457 ± 0.015
Floureanthene	4	ND	ND
Pyrene	4	3.819 ± 0.204	2.199 ± 0.039
Benzo (a) Anthrocene	4	4.076 ± 0.214	2.664 ± 0.034
Chrysene	4	3.498 ± 0.144	2.239 ± 0.005
Benzo (b) flouranthene	5	3.645 ± 0.309	1.538 ± 0.014
Benzo (k) flouranthene	5	3.650 ± 0.292	1.663 ± 0.012
Benzo (a) pyrene	5	ND	ND
Indo (1,2,3-cd) pyrene	6	ND	ND
Benzo (g,h,I) perylene	6	ND	ND
ΣPAH		38.224	32.801
ΣPAH carc.		14.869	8.104
ΣCOMB		18.687	10.303
ΣLPAH		20.84	22.499
ΣHPAH		18.687	10.303

ND – Not Detected

In this study, the GC-MS analyses of filter dust within the Bonny metropolis revealed the sources and distribution of polycyclic aromatic hydrocarbons about 7-11 PAHs compounds were detected in these samples. The total PAHs results at various sampling locations (32.801 to 38.224 mg/kg) were in order of magnitude as follows: Bonny Office > Bonny Residential. The total PAH in the studied area was higher than an earlier report from Lagos (Iwegbue *et*

al., 2020). Thus, the result depicts the contaminant level at varying sampling locations and the impact of various emissions of PAHs sources in the study area.

Naphthalene was observed to have a high concentration across the samples. Ihunwo and Ibezim-Ezeani (2021) have stated that the most available, and water-soluble PAHs in the environment is Naphthalene. It is also the simplest PAHs that are produced from coal tar through the process of crystallization and distillation (Phale *et al.*, 2019). However, the consistent industrial and exploration activities coupled with continuous gas flaring from the multi-national petroleum companies such as NLNG, Shell, and Mobil have contributed significantly to the concentration of PAHs within the Bonny metropolis. The findings in this study correspond to PAHs result reported by Qi *et al.*, (2014), and Shen *et al.*, (2020), in oil exploration settlements.

The proportion of LPAH was observed to be higher than HPAH in this study. This observation correlates with earlier studies (Ihunwo and Ibezim-Ezeani, 2021) but was contrary to the result of river sediments (Ihunwo *et al.*, 2019). LPAH are low molecular weight PAH which are volatile and primarily from diagenetic sources while HPAH is from pyrogenic sources owing to their high molecular weight. The predominance of LPAH indicates recent pollution or direct PAH input from sources such as the dry and wet atmospheric deposition. These PAHs are easily adsorbed on the surface of particulate matter through condensation and nucleation. Thus, the PAHs are intercepted by the A-C filter with the continuous circulation of air and thus accumulate in the dust of the filter.

Table 2. PAH Ratio of HVAC Filter Dust from Bonny Metropolis

PAH ratio	Bonny Office	Bonny Residential	Value range	Source	Reference
$\Sigma\text{PAHs}/\Sigma\text{PAH carc.}$	2.571	4.048			
LPAH/HPAH	1.115	2.184	< 1 > 1	Pyrogenic Petrogenic	Zhang <i>et al.</i> , 2008
$\Sigma\text{COMB}/\Sigma\text{PAHs}$	0.473	0.314	~ 1	Combustion	Ravindra <i>et al.</i> , 2008a
PHE/ANT	1.083	1.221	>10 <10	Petrogenic Pyrogenic	Budzinski <i>et al.</i> (1997)
FL/(FL + PYR)	0	0.7518	< 0.5 > 0.5	Petrol emissions Diesel emissions	Ravindra <i>et al.</i> , 2008b
ANT/(ANT + PHE)	0.480	0.450	< 0.1 > 0.1	Petrogenic Pyrogenic	Pies <i>et al.</i> , 2008
FLA/(FLA + PYR)	0.000	0.000	<0.4 0.4 - 0.5 >0.5	Petrogenic Fossil fuel combustion Grass, wood, coal	De La Torre-Roche <i>et al.</i> , 2009

BaA/(BaA + CHR)	0.538	0.543	<0.2 0.2 - 0.35 > 0.35	Petrogenic Coal Combustion and Vehicular emissions	Akyüz and Çabuk, 2010 Yunker <i>et al.</i> , 2002
BaP/(BaP + BeP)	0.000	0.000	< 0.2 > 0.35 ~0.5 < 0.5	Petrogenic Combustion Fresh particles Photolysis (aging of particles)	Oliveira <i>et al.</i> , 2011
IcdP/(IcdP + BghiP)	0.000	0.000	< 0.2 0.2 - 0.5 > 0.5	Petrogenic Petroleum combustion Grass, wood, and coal combustion	Yunker <i>et al.</i> , 2002
BbF/BkF	0.472	0.355	2.5 - 2.9	Aluminum smelter emissions	
BaP/BghiP	0.000	0.000	< 0.6 > 0.6	Non-traffic emissions Traffic emissions	Katsoyiannis <i>et al.</i> , 2007

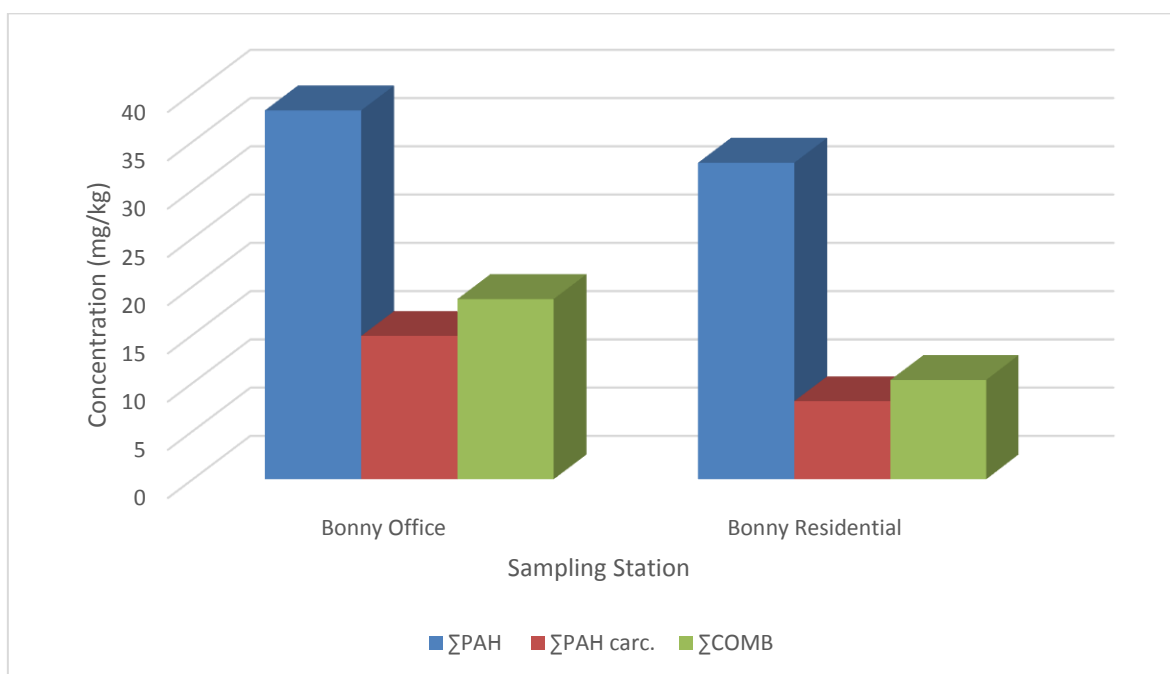


Fig.3. Total PAHs, Carcinogenic PAHs and Combustion PAHs

The graphical representation of the total PAHs concentration, combustion-related PAH, and the carcinogenic PAHs are shown in Fig.3 above. Among the PAHs, seven chemicals are probably human carcinogens which are benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthrax-

cene and indeno (1,2,3-cd)pyrene (USEPA, 1994). The sums of the carcinogenic PAHs (Σ PAH carc.) are also presented in Table 1. However, studies of individual PAHs in their complex mixtures have shown that individual PAHs interact metabolically in a plethora of ways resulting in additive, synergistic or antagonistic effects to cause its tumorigenic actions (Montizaan, 1989). Thus, PAHs with four rings or more have been presumably used in the prediction of the tumorigenic potency of a number of emission condensates such as in dust particulates. Adverse haematological effects have been reported arising from the injection of PAHs in earlier research (Anselstetter and Hempel, 1986). Data from animal studies indicate that several PAHs may induce several adverse effects including immunotoxicity, genotoxicity, carcinogenicity, and reproductive toxicity, and may also influence somatic mutation in the development of atherosclerosis (IARC, 1983; Wakabayashi, 1990).

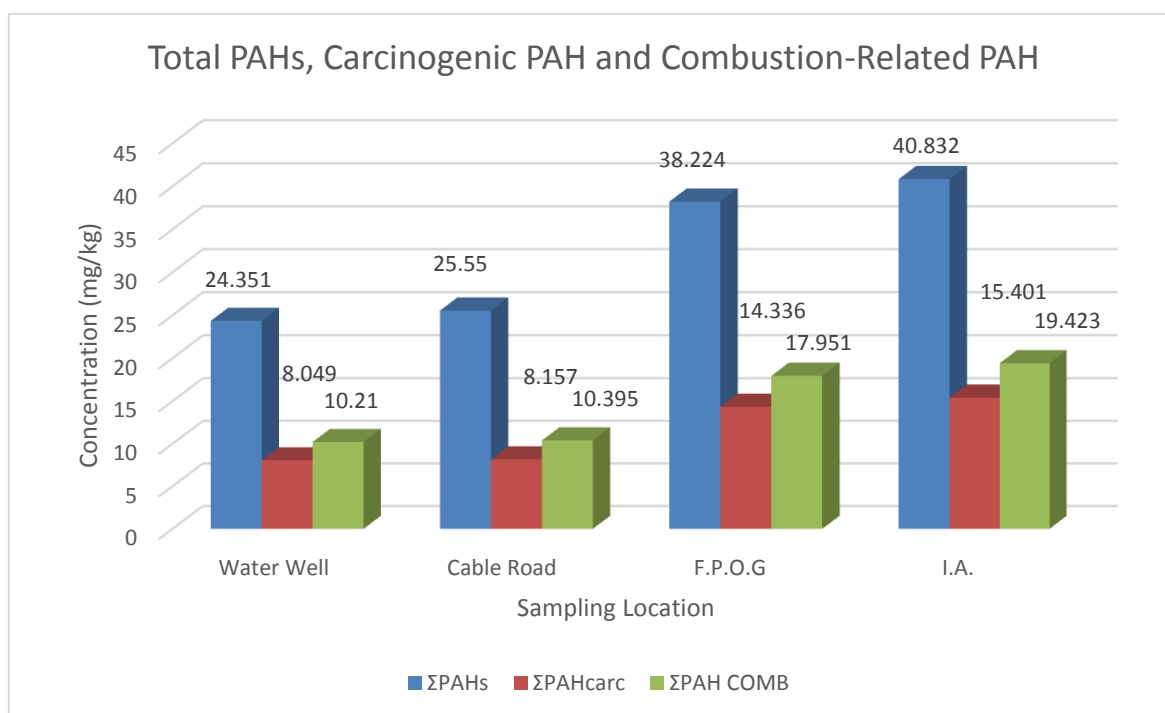


Fig.4. Summative Chart of PAH Constituent

Furthermore, combustion-related PAHs (COM) were observed to range between 0.233-18.687 mg/kg. It depicts the emission level of combustion-related industrial activities around the sampling location. Thus, a high percentage of combustion-related PAHs indicates the pyrogenic sourcing of PAHs as observed in the Bonny metropolis.

Table 3. Diagnostic PAHs Ratio of Filter Dust Bonny

PAHs Ratio	Water Well	Cable Road	F.P.O.G	Industrial Area	Value & Source	REF.
LPAH/HPAH	1.385	1.458	1.129	1.102	<1 Pyrogenic >1 Petrogenic	Zhang et al., 2008
Σ PAHcarc/ Σ PAH	0.331	0.319	0.375	0.377		

$\Sigma\text{PAH}_{\text{comb}}/\Sigma\text{PAH}$	0.419	0.407	0.470	0.476		
PHE/ANT	1.210	1.236	1.061	1.104	>10 Petrogenic <10 Pyrogenic	Budzinski et al. (1997)
ANT/(ANT + PHE)	0.453	0.447	0.485	0.475	<0.1 Petrogenic >0.1 Pyrogenic	Pies et al., 2008
BaA/(BaA + CHR)	0.539	0.547	0.561	0.515	<0.2 Petrogenic >0.35 Combustion and Vehicular Emission	Akyüz and Çabuk, 2010
BbF/BkF	0.922	0.927	0.994	1.003		

The LPAH/HPAH ranged 1.115-2.184 which were greater than 1 in all the sampling locations and PAHs could be attributed to sources of the petrogenic origin (Kerebba *et al.*, 2017; Ravindra *et al.*, 2008). However, Bonny metropolis has a relatively low LPAH/HPAH ratio owing to the negating influence of Pyrogenic activities taking place in the Industrial Area of the metropolis. Flt/(Flt+Pyr) ranged 0.0-0.7518 which depicts emission of high molecular weight petroleum product (Ravindra *et al.*, 2008b), Ant/(Ant+Phe) in Bonny was greater than 0.1 which also implied that PAHs had Pyrogenic sources.

Studies have identified the use of PAHs ratio in determining the source, distribution, and effect of PAHs which aids deductions from PAHs analyses (Costa and Sauer, 2005; Kerebba *et al.*, 2017). Table 2 represents the calculated PAHs ratio of filter dust in the Bonny metropolis. The ratios obtained were subsequently used in the evaluation of dust particulate matter. The lowest ratio was observed for Bonny Office location, thus having the highest carcinogen impact on humans within its densely concentrated environment when compared with the residential area. Diagnostic ratios (Table 3) are used to distinguish the originating sources of PAHs (Kerebba *et al.*, 2017). PAHs have similar physicochemical and stability properties in the environment having the same molar mass, aqueous solubilities, and octanol-water partition coefficient. Thus, the use of paired PAHs as a diagnostic source ratio suggests that PAHs with similar properties typically retain the same relative concentration in residues as in their sources (Kerebba *et al.*, 2017). Earlier research has used these ratios to predict the sources of PAHs since they are highly consistent (Yunker *et al.*, 2002; Kerebba *et al.*, 2017). In this study, the calculated ratio include Phe/Ant, Flt/(Flt+Pyr), Ant/(Ant+Phe), IcP/(IcP+BgP), BaA/(BaA+Chr) and LPAHs/HPAHs. Sampling from Bonny metropolis had a significantly high ratio. It implied that significantly high combustion-related activities take place within Bonny metropolis as evident in its continuous gas flaring activities in the petrochemical industries.

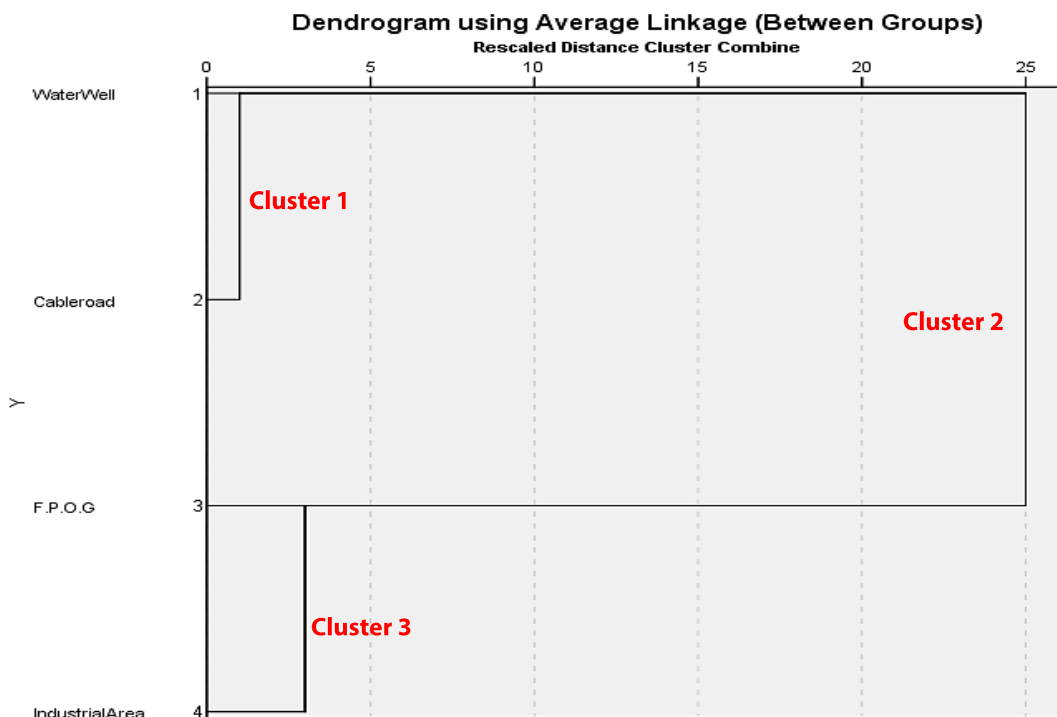


Fig.5. Dendrogram of Sampling Site

Cluster analysis also established the grouping across the sampling location into Cluster.

Table 4. Correlation between Sampling Sites

Pair	Location	N	Correlation	t	Sig. (2-tailed)
Pair 1	NLNG Water Well & Cable Road	16	.988	-1.892	.085
Pair 2	FPOG & IA	16	.981	-2.379	.037
Pair 3	NLNG Water Well & FPOG	16	.946	-6.491	.000
Pair 4	Cable Road & IA	16	.903	-5.845	.000
Pair 5	NLNG Water Well & IA	16	.904	-6.080	.000
Pair 6	Cable Road & FPOG	16	.944	-6.266	.000
Pair 7	Bonny Office & Bonny Residential	16	-0.111	0.815	0.432
Pair 8	Bonny Residential	16	0.635	-3.759	0.003

Bonny office and residential areas are negatively related and their concentration difference is insignificant (Table 4). Thus, the concentrations are tending toward opposing orders. The negative correlation implied that there might be additional uncommon sources of PAHs from the sampling location but its emission rates are similar.

However, residential areas in Bonny metropolis showed a strong positive correlation, and their concentrations are significantly different. This depicts a common source of PAHs emission such as domestic and food processing

emissions but these emissions have significantly different particle deposition rates, dilution areas and other trans-evaporation influences.

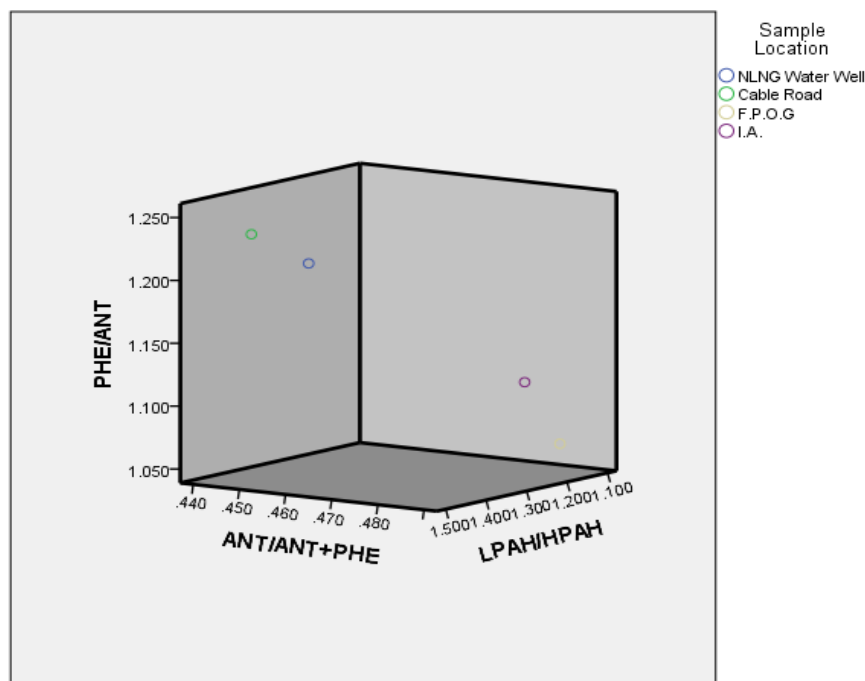


Fig.6. 3D Scatter Plot of Sampling Sites

Thus, considering the evaluated calculated ratios, a 3-D scatter plot of Phen/Anthra, Phe/(Phen+Anthra), and LPAH/HPAH are presented in Fig.6 above. The plot correlates with inference on the Pyrogenic source of PAHs in Bonny metropolis.

Conclusion

In this study, the GC-MS analyses of filter dust within Bonny metropolis have revealed the sources and distribution of polycyclic aromatic hydrocarbons.

Using the diagnostic ratio to evaluate the PAHs constituent, it has been suggested that Bonny metropolis has predominantly pyrogenic PAHs and is more hazardous.

Offices and Industrial areas in Bonny have more health impact on humans within its densely concentrated environment when compared with the residential areas.

The findings of this study are pivotal to the health of the residents of Bonny metropolis; it will also serve as a scientific record in time. Therefore, it is important to include PAHs monitoring in environmental assessment.

Recommendations

This study is not an end in itself. Upon this we make the following suggestions/recommendations for further studies:

[1] It is important for the Government to include PAHs monitoring in environmental assessment, especially in environments that have experienced considerable pollution events.

- [2] The general public should be enlightened on the health effect of PAH pollution on the environment.
- [3] The environmental agencies should enforce the law to regulate the emission of carbons, combustion activities and encourage the planting of trees within and around residential areas.
- [4] Residential areas should be located away from the location of industrial activities.
- [5] Further study should include surrounding villages.

Declarations

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Consent for publication

Authors declare that they consented for the publication of this research work.

Reference

- Adejuwon, J.O. (2012). Rainfall Seasonality in the Niger Delta Belt, Nigeria. *Journal of Geographical Regional Plan*, 5(2), 51-60.
- Akyüz, M., & Çabuk, H. (2010). Gaseparticle Partitioning and Seasonal Variation of Polycyclic Aromatic Hydrocarbons in the Atmosphere of Zonguldak, Turkey. *Science of the Total Environment*, 408(5550), 5558.
- Ali, M.U., Liu, G., Yousaf, B., Abbas, Q., Ullah, H., Munir, M.A.M., & Zhang, H. (2018). Compositional Characteristics of Black-Carbon and Nanoparticles in Air-Conditioner Dust from an Inhabitable Industrial Metropolis. *Journal of Clean Production*, 180, 34-42.
- Anselstetter, V. & Heimpel, H. (1986). Acute Hematotoxicity of Oral Benzo(a)Pyrene: the role of the Ah locus. *Acta haematologica Basel*, 76, 217-223.
- Armstrong, B. G., Hutchinson, E., Unwin, J., & Fletcher, T. (2004). Lung Cancer Risk After Exposure to Polycyclic Aromatic Hydrocarbons: A Review and Meta-Analysis. *Env. Health Perspectives*, 112, 970-978.
- Balabanova, D., Mckee, M., & Mills, A. (2012). Good Health at Low Cost: 25 years on. What makes a successful health system? *Reproductive Health Matters*, 20, 212-214. 10.2307/41714718.
- Blumer, M., Blumer, W., & Reich, T. (1977). Polycyclic Aromatic Hydrocarbons in Soils of a Mountain Valley: Correlation with Highway Traffic and Cancer Incidence. *Environmental Science and Technology*, 11, 1082-1084.
- Budzinski, H., Jones, I., Bellocq, J., Pierard, C. & Garrigues, P. (1997). Evaluation of Sediment Contamination by Polycyclic Aromatic Hydrocarbons in the Gironde Estuary. *Mar Chem* 58:85-97.
- Costa, H. J., & Sauer, T. C. (2005). Forensic Approaches and Considerations in Identifying PAH Background. *Environmental Forensics*, 6, 9-16. <https://doi.org/10.1080/15275920590913859>.
- Davis, J. J., & Gulson, B. L. (2005). Ceiling (attic) Dust: A "Museum" of Contamination and Potential Hazard. *Environmental Research*, 99, 177-94. 10.1016/j.envres.2004.10.011.

- De La Torre-Roche, R.J., Lee, W.Y., & Campos-Díaz, S.I. (2009). Soil-borne Polycyclic Aromatic Hydrocarbons in El Paso, Texas: Analysis of a Potential Problem in the United States/Mexico Border Region. *Journal of Hazardous Materials*, 163, 946-958.
- Diggs, D. L., Huderson, A. C., Harris, K. L., Myers, J. N., Banks, L. D., &Rekhadevi, P. V. (2011). Polycyclic Aromatic Hydrocarbons and Digestive Tract Cancers: A Perspective. *Journal of Environmental Science and Health, Part C*, 29, 324-357.
- Eisner, A.D., Richmond-Bryant, J., Hahn, I., Drake-Richman, Z.E., Brixey, L.A., Wiener, R.W., & Ellenson, W.D. (2009). Analysis of Indoor Air Pollution Trends and Characterization of Infiltration Delay Time using a Cross-Correlation Method. *Journal of Environmental Monitoring*, 11, 2201-2206.
- European Public Health Alliance (2009). Air, Water Pollution and Health Effects.
<https://epha.org/category/website-transfer/attic/old-environment/air-water-pollution-and-health-effects/>.
- Halse, A. K., Uggerud, H., Steinnes, E., & Schlabach, M. (2015). PAH Measurements in Air and Moss Around Selected Industrial Sites in Norway 2015. Norwegian Institute for Air Research, 30-37.
- Harvey, R. G. (1997). Polycyclic Aromatic Hydrocarbons. New York, NY: Wiley-VCH.
- Hsu, Y. M., Harner, T., Li, H., & Fellin, P. (2015). PAH Measurements in Air in the Athabasca Oil Sands Region. *Environmental Science and Technology*, 49, 5584-5592.
- Huang, Y., Ho, K.F., Ho, S.S.H., Lee, S.C., Yau, P.S., & Cheng, Y. (2011). Physical Parameters Effect on Ozone-Initiated Formation of Indoor Secondary Organic Aerosols with Emissions from Cleaning Products. *Journal of Hazardous Materials*, 192, 1787-1794.
- Ihunwo, O.C., & Ibezim-Ezeani, M.U. (2021). Distribution, Source Appropriation, and Human Health Risk Assessment of Polycyclic Aromatic Hydrocarbons due to Consumption of Callinectes Amnicola from Woji Creek in Sambreiro River. *Turkish Journal of Fisheries and Aquatic Sciences*, 21, 245-253.
- Ihunwo, O.C., Shahabinia, A.R., Udo, K.S., Bonnail, E., Onyema, M.O., Dibofori-Orji, A.N., & Mmom, P.C. (2019). Distribution of Polycyclic Aromatic Hydrocarbons in Woji Creek, in the Niger Delta. *Environmental Resource Community*, 1, 125001.
- International Agency for Research on Cancer (1998). Cadmium and Certain Compounds In: IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals on Humans. Chemicals, Industrial Processes and Industries Associated with Cancer in Humans. IARC Monographs, 1(29), 1-29.
- International Agency for Research on Cancer (2010). IARC monographs on the evaluation of carcinogenic risks to humans: Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. 92, 1-868.
- Iwegbue, C., Monday, E., Godswill, T., Osayanmo, E. & Bice, M. (2020). Occurrence, Sources and Exposure Risk of Polycyclic Aromatic Hydrocarbons (PAHs) in Street Dusts from the Nigerian Megacity, Lagos. *Polycyclic Aromatic Compounds*. 1-21. 10.1080/10406638.2020.1716027.
- Kang, D.H., Choi, D.H., Lee, S.M., Yeo, M.S., & Kim, K.W. (2010). Effect of Bake-Out on Reducing VOC Emissions and Concentrations in a Residential Housing Unit with a Radiant Floor Heating System. *Journal of Building and Environment*, 45, 1816-1825.

- Katsoyiannis, A., Terzi, E., & Cai, Q.Y. (2007). On the use of PAH Molecular Diagnostic Ratios in Sewage Sludge for the Understanding of the PAH Sources. *Chemosphere*, 69, 1337e1339.
- Kerebba, N., Patrick, S., Kwetegyeka, J., Arinaitwe, K., & Wasswa, J. (2017). Concentrations and Source Apportionment of Polycyclic Aromatic Hydrocarbons in Sediments from the Uganda side of Lake Victoria. *Environmental Science: Processes & Impacts*, 19. 10.1039/C7EM00017K.
- Laitinen, A., Michaux, A., & Aaltonen, O. (1994). Soil Cleaning by Carbon-Dioxide Extraction - A Review. *Environmental Technology*, 15, 715-727.
- Landrigan, P. J., Fuller, R., Acosta, N., Adeyi, O., Arnold, R., Basu, N. N., Baldé, A. B., Bertollini, R., Bose-O'Reilly, S., Boufford, J. I., Breyse, P. N., Chiles, T., Mahidol, C., Coll-Seck, A. M., Cropper, M. L., Fobil, J., Fuster, V., Greenstone, M., Haines, A., Hanrahan, D., & Zhong, M. (2018). The Lancet Commission on Pollution and Health. *Lancet* (London, England), 391(10119), 462–512.
- Liu, K., Heltsley, R., Zou, D., Pan, W. P., & Riley, J. T. (2002). Polyaromatic Hydrocarbon Emissions in fly Ashes from an Atmospheric fluidised Bed Combustor using Thermal Extraction Coupled with GC/TOF/MS. *Energy Fuels*, 16, 330-337.
- Loganathan, P., Vigneswaran, S., Kandasamy, J., & Bolan, N. (2014). Removal and Recovery of Phosphate from Water Using Sorption. *Critical Reviews in Environmental Science and Technology*, 44.
- Manisalidis, I., Stavropoulou, E., Stavropoulos, A., & Bezirtzoglou, E. (2020). Environmental and Health Impacts of Air Pollution: A Review. *Frontiers in Public Health*, 8, 14. doi: 10.3389/fpubh.2020.00014
- Montizaan, G.K. (1989). Integrated Criteria Document PAH: Addendum. (758474011), Bilthoven, National Institute of Public Health and Environmental Protection (RIVM).
- Nigeria Liquefied Natural Gas (2005) Environmental Impact Assessment for the Nigeria LNG Six Project Bonny Island, (1&2). Ecosphere Nigeria and Babsal & Company.
- Niranjan, R., & Thakur, A. K. (2017). The Toxicological Mechanisms of Environmental Soot (Black Carbon) and Carbon Black: Focus on Oxidative Stress and Inflammatory Pathways. *Frontiers in immunology*, 8, 763. <https://doi.org/10.3389/fimmu.2017.00763>.
- Norback, D., Wieslander, G., Zhang, X., & Zhao, Z. (2011). Respiratory Symptoms, Perceived Air Quality and Physiological Signs in Elementary School Pupils in Relation to Displacement and Mixing Ventilation System: An Intervention Study. *Indoor Air*, 21, 427-437.
- NPC (2006). National Population Commission.
- Oliveira, C., Martins, N., Tavares, J., Pio, C., Cerqueira, M., Matos, M., Silva, H., Oliveira, C., & Camoes, F. (2011). Size Distribution of Polycyclic Aromatic Hydrocarbons in a Roadway Tunnel in Lisbon, Portugal. *Chemosphere*, 2011, 01.011. <http://dx.doi.org/10.1016/j.chemosphere.2011.01.011>.
- Oloyede, M. & Ede, P.N. (2020). Source Apportionment and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Black Carbon Monitored in Port Harcourt, Rivers State, Nigeria. *International Journal of Innovative Science and Research Technology*. 5(8), 653-663.

- Omidvarborna, H., Kumar, A., & Kim, D-S. (2015). Recent Studies on Soot Modeling for Diesel Combustion. *Renewable and Sustainable Energy Reviews*, 48, 635-647. 10.1016/j.rser.2015.04.019.
- Ong, S.T., Ayoko, G.A., Kokot, S.K. & Morawska, L.M. (2007). Polycyclic Aromatic Hydrocarbons in House Dust Samples: Source identification and apportionment. In (14th) international IUAPPA world congress.
- Petrick, L.M., Sleiman, M., Dubowski, Y., Gundel, L.A., & Destailats, H. (2011). Tobacco Smoke Aging in the Presence of Ozone: A Room-Sized Chamber Study. *Atmospheric Environment*, 45, 4959-4965.
- Phale, P.S., Sharma, A., & Gautam, K. (2019). Microbial Degradation of Xenobioticslike Aromatic Pollutants from the Terrestrial Environments. In M.N.V. Prasad, M. Vithanage, & A.B.T.-P. and P.C.P.W.M. and T.T. Kapley (Eds.), *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology. Emerging Contaminants and Micro Pollutants* (259-278). Butterworth-Heinemann.
- Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., & Hofmann, T., (2008). Characterization and Source Identification of Polycyclic Aromatic Hydrocarbons (PAHs) in River Bank Soils. *Chemosphere* 72, 1594e1601.
- Pongpiachan, S., Tipmanee, D., Deelaman, W., Muprasit, J., Feldens, P., & Schwarzer, K. (2013). Risk Assessment of the Presence of Polycyclic Aromatic Hydrocarbons (PAHs) in Coastal Areas of Thailand affected by the 2004 Tsunami. *Marine Pollution Bulletin*, 76, 370-378.
- Qi, H., Li, W. L., Zhu, N. Z., Ma, W. L., Liu, L. Y., Zhang, F., & Li, Y. F. (2014). Concentrations and Sources of Polycyclic Aromatic Hydrocarbons in Indoor Dust in China. *Science of the Total Environment*, 491-492, 100-107.
- Rajpara, R. K., Dudhagara, D. R., Bhatt, J. K., Gosai, H. B., & Dave, B. P. (2017). Polycyclic Aromatic Hydrocarbons (PAHs) at the Gulf of Kutch, Gujarat, India: Occurrence, Source Apportionment, and Toxicity of PAHs as an Emerging Issue. *Marine Pollution Bulletin*, 119, 231-238. doi: 10.1016/j.marpolbul.2017.04.039.
- Ravindra, K., Sokhi, R., & Van Greiken, R. (2008). Atmospheric Polycyclic Aromatic Hydrocarbons: Source Attributions, Emission Factor and Regulations. *Atmospheric Environment*, 42(13), 2895-2921.
- Ravindra, K., Stranger, M., & Van Grieken, R. (2008). Chemical Characterization and Multivariate Analysis of Atmospheric Particulate Matter (2.5) Particles. *Journal of Atmospheric Chemistry*, 59, 199-218.
- Ravindra, K., Wauters, E., & Van Grieken, R. (2008b). Variation in Particulate PAHs Levels and their Relation with the Transboundary Movement of the Air Masses. *Science of the Total Environment*, 396, 100e110.
- Saeedi, M., Li, L. Y., & Salmanzadeh, M. (2012). Heavy Metals and Polycyclic Aromatic Hydrocarbons: Pollution and Ecological Risk Assessment in Street Dust of Tehran. *Journal of Hazardous Materials*, 15, 227-228: 9-17. doi: 10.1016/j.jhazmat.2012.04.047.
- Shamsipur, M., Gholivand, M. B., Shamizadeh, M., & Hashemi, P. (2015). Preparation and Evaluation of a Novel Solid-Phase MicroextractionFiber Based on Functionalized Nanoporous Silica Coating for Extraction of Polycyclic Aromatic Hydrocarbons from Water Samples Followed by GC-MS Detection. *Chromatographia*, 78, 795-803.
- Shen, G., Zhang, Y., Wei, S., Chen, Y., Yang, C., Lin, P., Xie, H., Xue, M., Wang, X., & Tao, S. (2014). Indoor/Outdoor Pollution Level and Personal Inhalation Exposure of Polycyclic Aromatic Hydrocarbons through Biomass Fuelled Cooking. *Air Quality, Atmosphere & Health*, 7, 449-458.

- Sun, L., & Zang, S. (2013). Relationship between Polycyclic Aromatic Hydrocarbons (PAHs) and Particle Size in Dated Core Sediments in Lake Lianhuan, Northeast China. *Science of the Total Environment*, 461-462, 180-187.
- Teng, J., Vaze, J., Chiew, F., Wang, B., & Perraud, J. M. (2012). Estimating the Relative Uncertainties Sourced from GCMs and Hydrological Models in Modeling Climate Change Impact on Runoff. *Journal of Hydrometeorology*, 13, 122-139. 10.1175/JHM-D-11-058.1.
- Tripathi, K. A., Sudhir, N., Harsh, K., & Gupta, N. (2007). Fungal Treatment of Industrial Effluents: A Mini-Review, 78-80.
- USEPA (1994). A Plain English Guide to the EPA Part 503 Biosolids Rule, USEPA Rep. 832/R-93/003, USEPA, Washington, DC, USA, 1994.
- Verma, R., Patel, K. S., & Verma, S. K. (2015). Indoor Polycyclic Aromatic Hydrocarbon Concentration in Central India. *Polycyclic Aromatic Compounds*, 36, 1-17.
- Vuković, G., AničićUrošević, M., Razumenić, I., Kuzmanoski, M., Pergal, M., Škrivanj, S., & Popović, A. (2014). Air Quality in Urban Parking Garages (PM10, Major and Trace Elements, PAHs): Instrumental Measurements Vs. Active Moss Biomonitoring. *Atmospheric Environment*, 85, 31-40.
- Wakabayashi, K. (1990): International Commission for Protection against Environmental Mutagens and Carcinogens. ICPEMC Working Paper 7/1/3. Animal studies suggesting involvement of mutagen/ carcinogen exposure in atherosclerosis. *Mutation research*, 239,181-187.
- Wang, Z., Wang, S., Nie, J., Wang, Y., & Liu, Y. (2017). Assessment of Polycyclic Aromatic Hydrocarbons in Indoor Dust from Varying Categories of Rooms in Changchun City, Northeast China. *Environmental Geochemistry and Health*, 39(1), 15-27. <https://doi.org/10.1007/s10653-016-9802-8>.
- White, A. J., Teitelbaum, S. L., Stellman, S. D., Beyea, J., Steck, S. E., Mordukhovich, I., McCarty, K. M., Ahn, J., Rossner, P., Jr, Santella, R. M., & Gammon, M. D. (2015). Indoor Air Pollution Exposure from use of Indoor Stoves and Fireplaces in Association with Breast Cancer: A Case-Control Study. *Environmental Health: A Global Access Science Source*, 13, 108. <https://doi.org/10.1186/1476-069X-13-108>.
- Xing, S., Wallmeroth, N., Berendzen, K. W., & Grefen, C. (2016). Techniques for the Analysis of Protein-Protein Interactions in Vivo. *Plant Physiology*, 171(2), 727-758, <https://doi.org/10.1104/pp.16.00470>.
- Yao, Y., Xiong, J., Liu, W., Mo, J., & Zhang, Y. (2011). Determination of the Equivalent Emission Parameters of Wood-Based Furniture by Applying C-history Method. *Atmospheric Environment*, 45, 5602-5611.
- Yu, H., Kim, D., & Gundersen, T. (2019). A Study of Working Fluids for Organic Rankine Cycles (ORCs) Operating Across and Below Ambient Temperature to Utilize Liquefied Natural Gas (LNG) Cold Energy. *Energy*, 167, 730-739.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., & Sylvestre, S., (2002). PAHs in the Fraser River Basin: a Critical Appraisal of PAH Ratios as Indicators of PAH Source and Composition. *Organic Geochemistry*, 33, 489-515.

Zhang, W., Zhang, S., Wan, C., Yue, D., Ye, Y., & Wang, X., (2008). Source Diagnostics of Polycyclic Aromatic Hydrocarbons in Urban Road Runoff, Dust, Rain and Canopy Throughfall. *Environmental Pollution*, 153, 594e601.

Zhang, Z.-H., & Balasubramanian, R. (2016). Investigation of Particulate Emission Characteristics of a Diesel Engine Fueled with Higher Alcohols/Biodiesel Blends. *Applied Energy*, 16, 71-80. doi: 10.1016/j.apenergy.2015.10.173.